

REMARKS

Claims 1-10 are pending. Claims 1, 2, and 4 are under examination. The Examiner argues that the other claims are subject to a Restriction Requirement. The following subheading numbers correspond to the paragraph numbers in the Office Action.

2-3 Restriction Requirement

The Examiner's argument in paragraph 2 and elsewhere in the last Office Action that claims 3 and 5-10 are subject to a Restriction Requirement is traversed. It is respectfully submitted that these claims should be examined together with claims 1, 2 and 4 since there would not be an undue burden on the Examiner to do so.

The use by the Examiner of the acronym "ODP" in the last Office Action on page 3 at line 5 is not understood.

4-6 Double Patenting Issues

The provisional obvious-type double patenting rejection is traversed.

The Examiner's reference to a certain passage in USP 2003/0232940 A1 (Komoriya) is not understood. **The Examiner refers to page 27 of Komoriya in the last Office Action on page 5 at line 5. However, Komoriya has no page 27 but only has 20 pages.**

Perhaps the Examiner is referring to the following paragraph of Komoriya:

[0118] The polymerization or copolymerization method for obtaining the target polymer (copolymer) is not particularly limited. For example, it is preferable to use radical polymerization or ionic polymerization. In some cases, it is also possible to use coordinated anionic polymerization or living anionic polymerization.
[US2003/0232940 A1; page 9; emphasis supplied]

The above cited passage of Komoriya is in the specification and not the claims and is not relevant to any double patenting issue. None of the claims of Komoriya recite a polydispersity index of 1 to 1.2. For purposes of discussion, even if the polymers claimed in Komoriya could have polydispersibility index of 1 to 1.20, it is also possible that they could have a polydispersibility index falling outside of the range of 1 to 1.20. In order to prepare a polymer having the claimed polydispersibility index, the polymerization conditions must be carefully controlled. The claims of Komoriya do not teach how to prepare the polymer claimed in the present application. Therefore, the provisional obvious-type double patenting rejection should be withdrawn.

9-15 Issues under 35 U.S.C. 103

In summary all rejections for alleged obviousness under 35 U.S.C. 103 are traversed. No reference describes any polymer having a polydispersibility index of 1 to 1.20. Neither is it

obvious to modify any of the cited references to produce the claimed fluorinated polymer.

The rejection in paragraphs 7-9 of claims 1, 2 and 4 as obvious over USP 2002/0164538 A1 (Allen) or USP 2002/0155376 A1 (Hashimoto) each individually in view of Sprague cited in paragraph 9 on page 6 of the last Office Action is traversed. Neither Allen nor Hashimoto nor Sprague disclose a polymer having a polydispersibility index of 1 to 1.20 as required by all pending claims. Neither do any of these three references render such a polymer obvious to the skilled artisan.

The rejection in paragraph 10 on page 6 of the last Office Action of claims 1, 2, and 4 as obvious over USP 3,179,640 (Middleton) in view of Sprague and either Allen or Hashimoto is traversed. None of these references disclose a polymer having the polydispersibility index as required by the pending claims.

The rejection in paragraph 11 on page 7 of the last Office Action of claims 1, 2, and 4 as obvious over Komoriya is traversed.

Summary

None of the cited references discloses or teaches the inventive fluorinated polymer having a polydispersity index of 1 to 1.20. The claimed polymer having a polydispersity index of 1 to 1.20 produces a polymer which has a higher glass transition temperature as compared with a polymer having a higher

polydispersity index of more than 1.20. The glass transition temperature influences the prebaking temperature and post exposure bake (PEB) temperature. Accordingly, the inventive fluorinated polymer having a polydispersity index of 1 to 1.20 with its attendant higher glass transition temperature exerts an excellent and non-obvious effect on increasing prebake temperature and PEB temperature, resulting in easy control of the acid diffusion property and the deblocking reactivity. Even if all of the cited references are considered in combination, with hindsight, they fail to teach an essential feature of the claimed invention. Therefore, a *prima facie* case of obviousness has not been established.

Komoriya et al. is not prior art against the present application. Although Komoriya et al. is potentially available as prior art under 35 U.S.C. 102(e) based on its earlier U.S. filing date of December 11, 2002, Applicants are submitting herewith a verified English translation of JP 2002-222955 which has a filing date of July 31, 2002. The claims of the present application are supported by JP 2002-222955 and therefore Komoriya et al. is no longer available as prior art. However, even if Komoriya et al. were prior art, it does not teach the polydispersibility index limitation in the present claims.

The claimed invention is not obvious in view of the cited references.

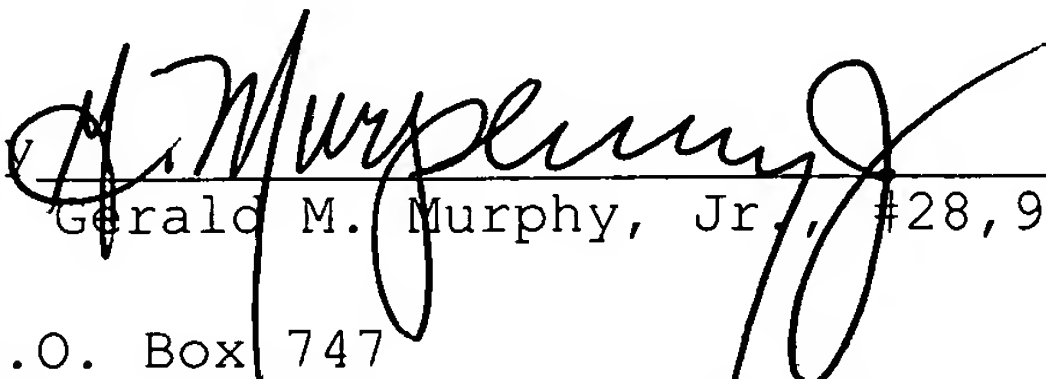
Conclusion

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact David R. Murphy (Reg. No. 22,751) at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. §§ 1.16 or 1.17; particularly, extension of time fees.

Respectfully submitted,

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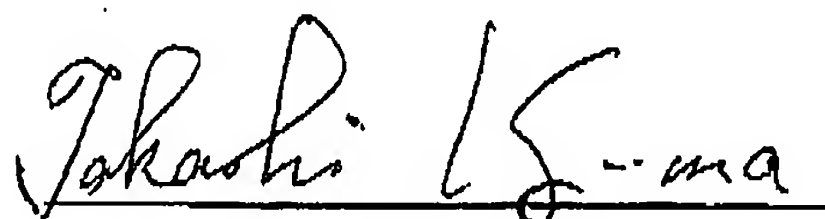
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Attachment: Verified English Translation of JP 2002-222955

BEST AVAILABLE COPY**C E R T I F I C A T I O N**

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 31st of July, 2002 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 21st day of April, 2005

A handwritten signature in cursive script, appearing to read 'Takashi Kojima', is written over a horizontal line.

Takashi KOJIMA



(Translation)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: July 31, 2002

Application Number: Japanese Patent Application
No. 2002-222955

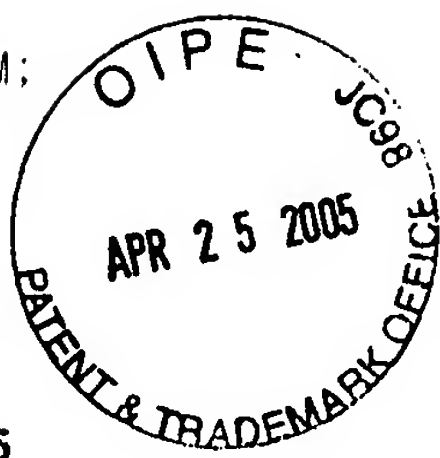
Applicant(s): Central Glass Co., Ltd.
Shin-Etsu Chemical Co., Ltd.

July 9, 2003

Commissioner,
Patent Office

Shinichiro OTA
(sealed)

Certificate No. 2003-3055291



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2002-222955

[Paper] APPLICATION FOR PATENT

[Reference Number] 02K1211

[Application Date] July 31, 2002

[Destination] The Commissioner of the Patent Office

[International Patent Classification]
G03F 07/004
G03F 07/039

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Agent of Central Glass Co., Ltd. (Applicant)

[Official Fee]

[Deposit Account Number]

013837

[Amount of Fee]

21000

[List of Documents Attached]

[Document]

Specification

1

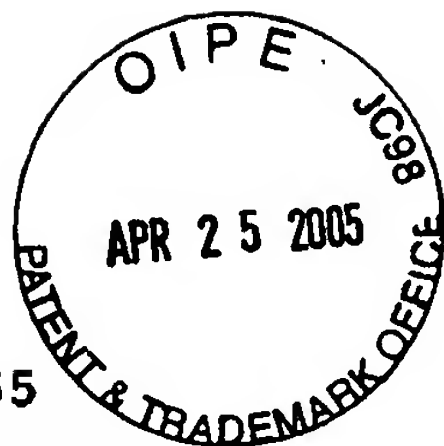
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Abstract

1

[Necessity of Proof]

Yes



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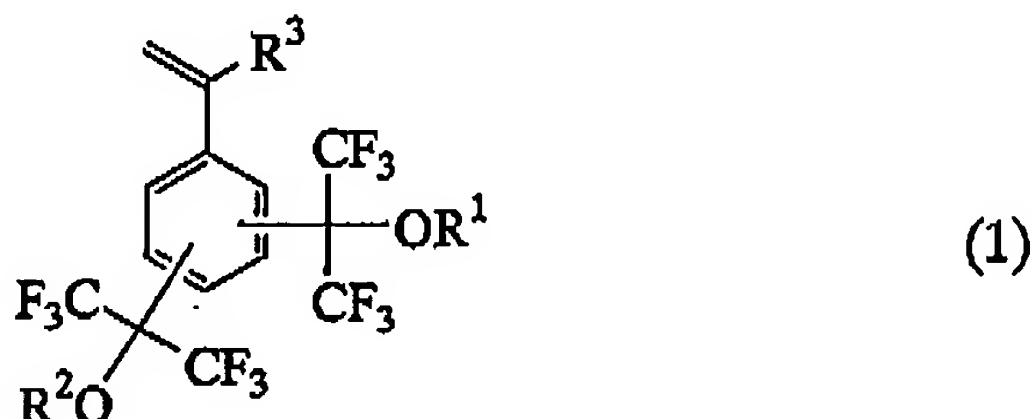
2002-222955

[SPECIFICATION]

[TITLE OF THE INVENTION] Fluorinated Polymer

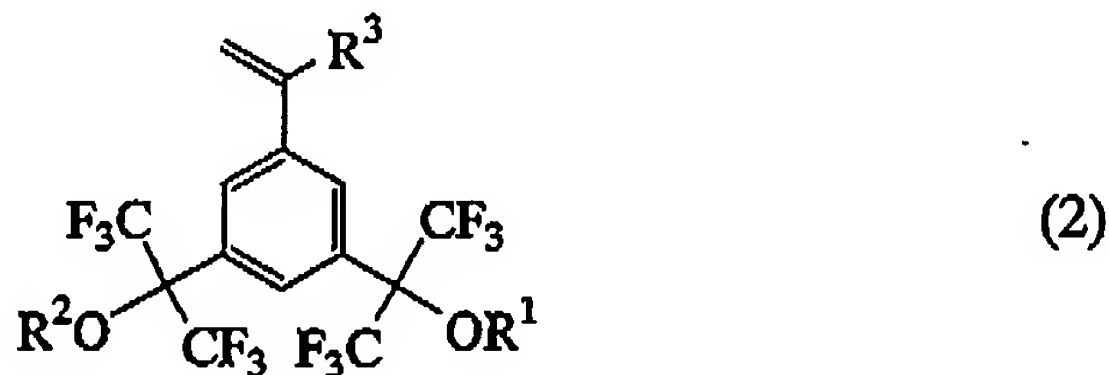
[CLAIMS]

- 5 [Claim 1] A fluorinated polymer obtained by living anion polymerization of a monomer having the general formula (1):



- wherein R¹ and R² each are an acid labile group and R³ is hydrogen or methyl, and having a polydispersity index of 1 to 1.20.

- 10 [Claim 2] The fluorinated polymer of claim 1 wherein the monomer has the general formula (2):



- wherein R¹ and R² each are an acid labile group and R³ is hydrogen or methyl.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

- This invention relates to fluorinated polymers having an appropriate polydispersity index for use in chemically amplified resist compositions for forming fine-circuitry patterns on the surface of semiconductor devices using ultraviolet or vacuum ultraviolet radiation.

[0002]

[Prior Art]

In the drive for higher integration and operating speeds in LSI devices, the pattern rule is made drastically finer. The rapid advance toward finer pattern rules is grounded on the development of a projection lens with an increased NA, a resist material with improved performance, and exposure light of a shorter wavelength. To the demand for a resist material with a higher resolution and sensitivity, positive resist materials of the chemical amplification type utilizing as a catalyst an acid generated upon light exposure are effective. They now become predominant resist materials especially adapted for deep UV lithography (as disclosed in JP-B 2-27660 and JP-A 63-27829).

15 [0003]

The change-over from i-line (365 nm) to shorter wavelength KrF (248 nm) brought about a significant innovation. Resist materials adapted for KrF excimer lasers enjoyed early use on the 0.30 micron process, passed through the 0.25 micron rule, and currently entered the mass production phase on the 0.18 micron rule. Engineers have started investigation on the 0.10 micron rule or below, with the trend toward a finer pattern rule being accelerated.

[0004]

25 ArF (193 nm) is expected to enable miniaturization of the design rule to 0.13 μm or less. Since conventionally used novolac resins and polyvinylphenol resins have very strong absorption in proximity to 193 nm, they cannot be used as the base resin for resists. To ensure transparency and dry etching resistance, some engineers investigated acrylic and alicyclic (typically cycloolefin) resins (as disclosed in JP-A 9-73173, JP-A 10-10739, JP-A 9-230595 and WO 97/33198).

[0005]

35 With respect to F_2 (157 nm) which is expected to enable further miniaturization to 0.10 μm or less, more difficulty arises in insuring transparency because it was found that

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acrylic resins, which serve as the base polymer for ArF, are not transmissive to light at all and those cycloolefin resins having carbonyl bonds have strong absorption. It was also found that polyvinylphenol used as the base polymer for KrF has a window for absorption in proximity to 160 nm, so the transmittance is somewhat improved, but far below the practical level.

[0006]

[Problem to be Solved by the Invention]

For the preparation of polymers for use in the UV and vacuum UV wavelength regions, many processes utilizing radical polymerization and vinyl addition polymerization have been reported. The polymers obtained by these processes have a wide molecular weight distribution or polydispersity index. When such a polymer is used in resist, a low molecular weight fraction of the polymer gasifies during vacuum steps in the wafer processing process to give rise to problems including a loss of vacuum and contamination of the process atmosphere, and the dissolution rate of the polymer undesirably varies owing to an uneven molecular weight distribution. As a result, the patterning process is reproducible with difficulty, often forming uneven patterns.

[0007]

The present invention has been done in view of the above circumstances. The invention provides a novel polymer having a high transmittance to ultraviolet radiation, especially KrF beam (248 nm) and F₂ excimer laser beam (157 nm), a high sensitivity and high etching resistance.

[0008]

[Means for Solving the Problem]

The present inventors have earnestly studied in order to attain the above object and develop a fluorinated polymer suitable for use in resist compositions, especially positive resist compositions having sensitivity to ultraviolet radiation, especially KrF beam or F₂ excimer laser beam and improved properties. As a result, the inventors have found

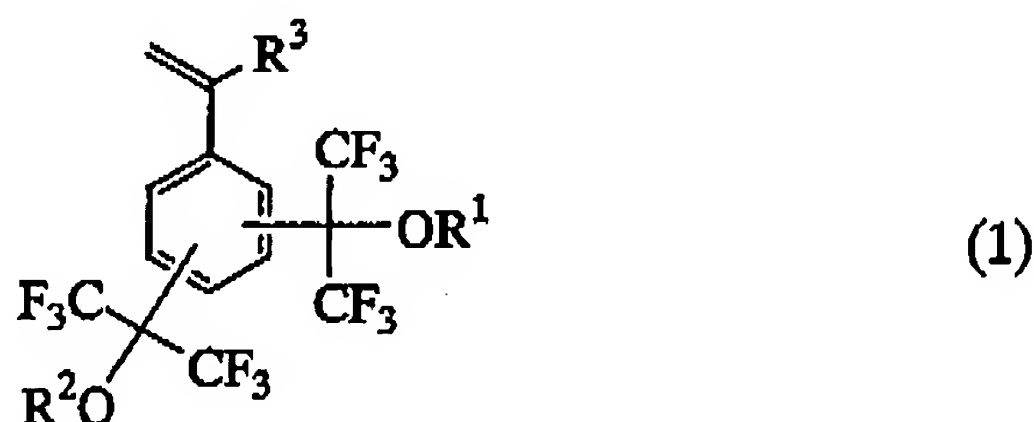
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that a fluorinated polymer having a polydispersity index (Mw/Mn) in a narrow range of about 1 to 1.20 can be prepared by subjecting an aromatic monomer having a sufficient fluorine content to living anion polymerization rather than conventional radical polymerization and cationic polymerization. Thus the present invention has been completed.

[0009]

The present invention is the following fluorinated polymer. A fluorinated polymer obtained by living anion polymerization of a monomer having the general formula (1):

[0010]

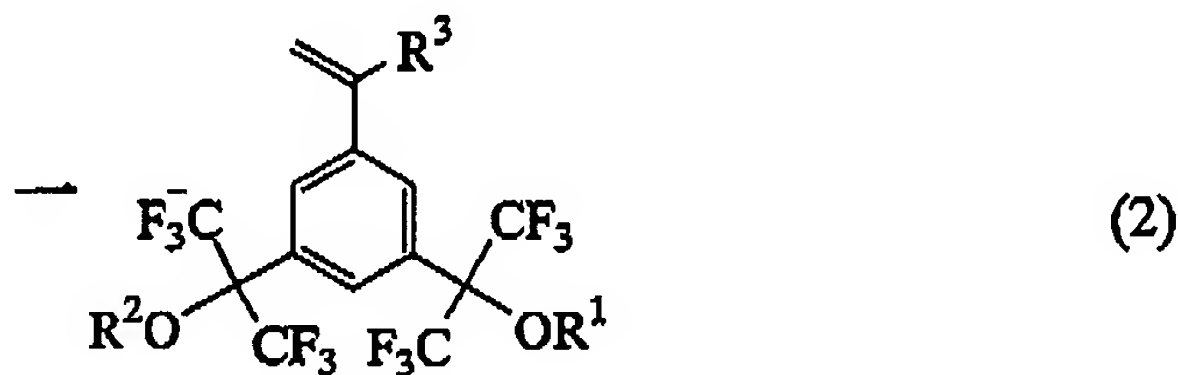


[0011]

wherein R¹ and R² each are an acid labile group and R³ is hydrogen or methyl, and having a polydispersity index of 1 to 1.20.

A fluorinated polymer described above obtained by using a monomer having the general formula (2):

[0012]



[0013]

wherein R¹ and R² each are an acid labile group and R³ is hydrogen or methyl.

[0014]

The following is the detailed description of the present invention.

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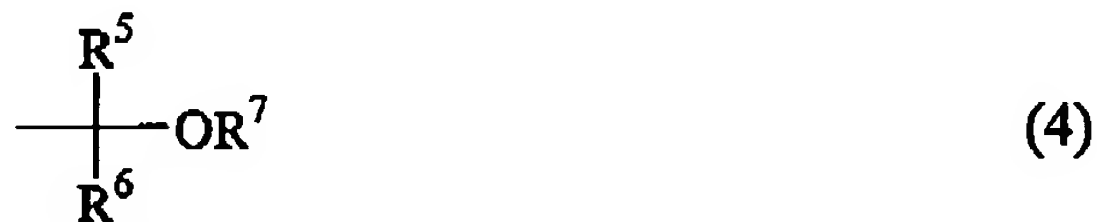
The fluorinated polymer of the invention is obtained by living anion polymerization of a monomer having the general formula (1), preferably formula (2).

In formulae (1) and (2), R^1 and R^2 may represent the same or different acid labile groups and be used in any desired combination. Preferred are acid labile groups which do not affect living anion polymerization and are compliant with the purpose that some or all of the acid labile groups are to be eliminated after polymerization.

10 [0015]

In the invention, the acid labile groups represented by R^1 and R^2 are preferably selected from the groups of the general formulae (3) to (5).

[0016]



15

[0017]

In the general formula (3), R^4 is a tertiary alkyl group of 4 to 20 carbon atoms, preferably 4 to 15 carbon atoms, an oxoalkyl group of 4 to 20 carbon atoms or a group of formula (5). Exemplary tertiary alkyl groups are tert-butyl, tert-amyl, 1,1-diethylpropyl, 1-ethylcyclopentyl, 1-butylcyclopentyl, 1-ethylcyclohexyl, 1-butylcyclohexyl, 1-ethyl-2-cyclopentenyl, 1-ethyl-2-cyclohexenyl, and 2-methyl-2-adamantyl. Exemplary oxoalkyl groups are 3-oxocyclohexyl, 4-methyl-2-oxooxan-4-yl, and 5-methyl-5-oxoxolan-4-yl. Letter g is an integer of 0 to 6.

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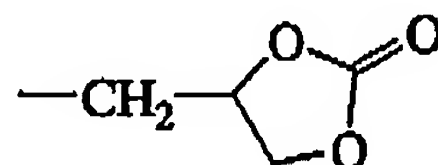
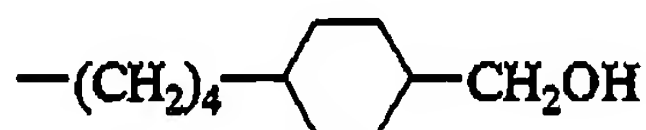
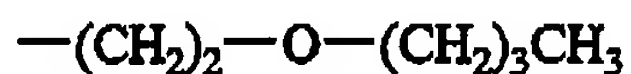
[0018]

Illustrative examples of the acid labile groups of the general formula (3) include tert-butoxycarbonyl, tert-butoxycarbonylmethyl, tert-amylloxycarbonyl, tert-amylloxycarbonylmethyl, 1,1-diethylpropyloxycarbonyl, 1,1-diethylpropyloxycarbonylmethyl, 1-ethylcyclopentyloxycarbonyl, 1-ethylcyclopentyloxycarbonylmethyl, 1-ethyl-2-cyclopentenylloxycarbonyl, 1-ethyl-2-cyclopentenylloxycarbonylmethyl, 1-ethoxyethoxycarbonylmethyl, 2-tetrahydropyranyloxycarbonylmethyl, and 2-tetrahydrofuranyloxycarbonylmethyl.

[0019]

In the general formula (4), R⁵ and R⁶ are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, cyclopentyl, cyclohexyl, 2-ethylhexyl and n-octyl. R⁷ is a monovalent hydrocarbon group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, which may have a hetero atom (e.g., oxygen atom), for example, straight, branched or cyclic alkyl groups, and such groups in which some hydrogen atoms are replaced by hydroxyl, alkoxy, oxo, amino or alkylamino groups. Illustrative examples of the substituted alkyl groups are given below.

[0020]



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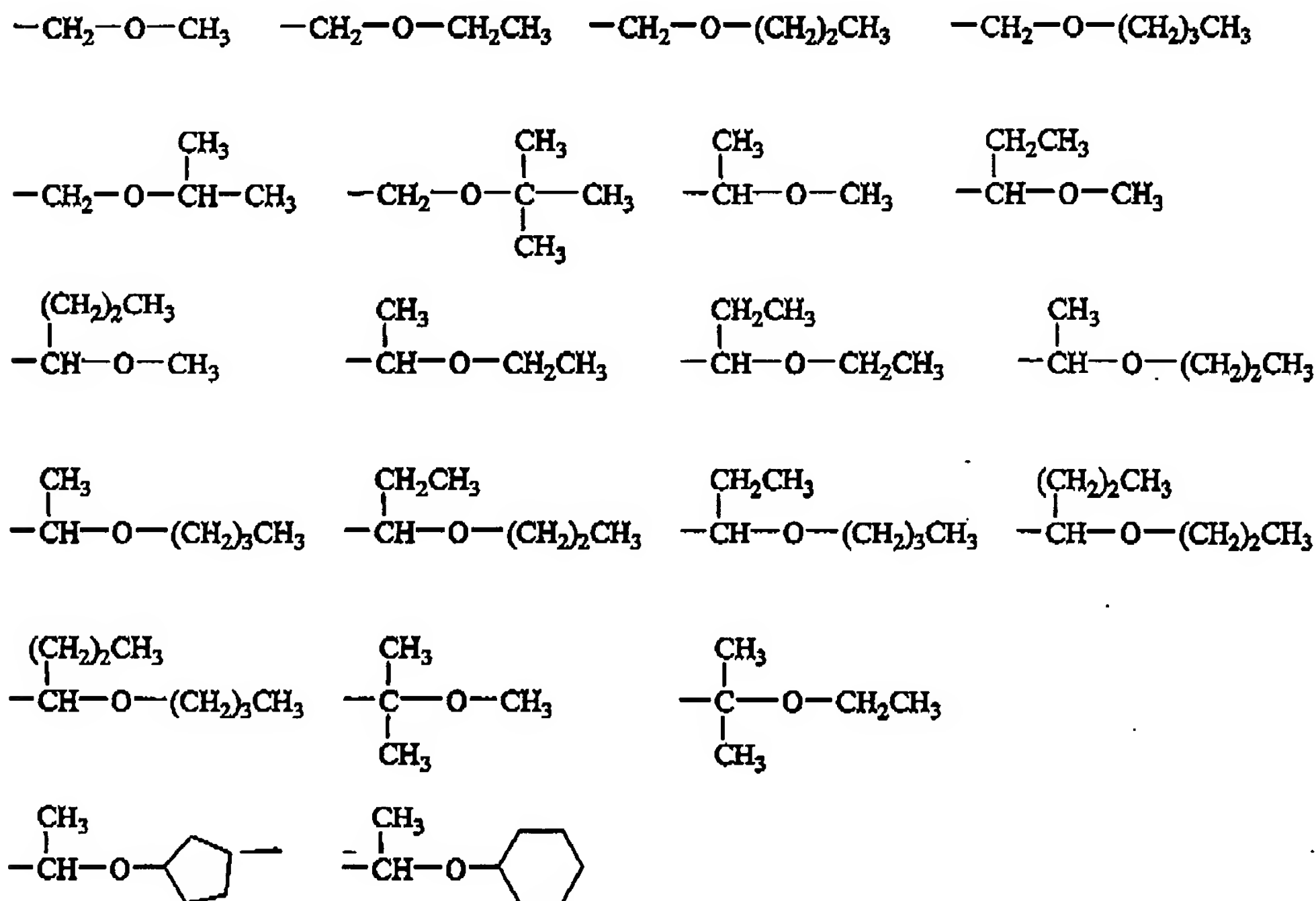
[0021]

A pair of R^5 and R^6 , a pair of R^5 and R^7 , or a pair of R^6 and R^7 , taken together, may form a ring. Each of R^5 , R^6 and R^7 is a straight or branched alkylene group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, when they form a ring.

[0022]

Of the acid labile groups of the general formula (4), illustrative examples of the straight or branched groups are given below.

[0023]



[0024]

Of the acid labile groups of the general formula (4), illustrative examples of the cyclic groups include tetrahydrofuran-2-yl, 2-methyltetrahydrofuran-2-yl, tetrahydropyran-2-yl and 2-methyltetrahydropyran-2-yl. Preferred among the groups of formula (4) are ethoxyethyl, butoxyethyl and ethoxypropyl.

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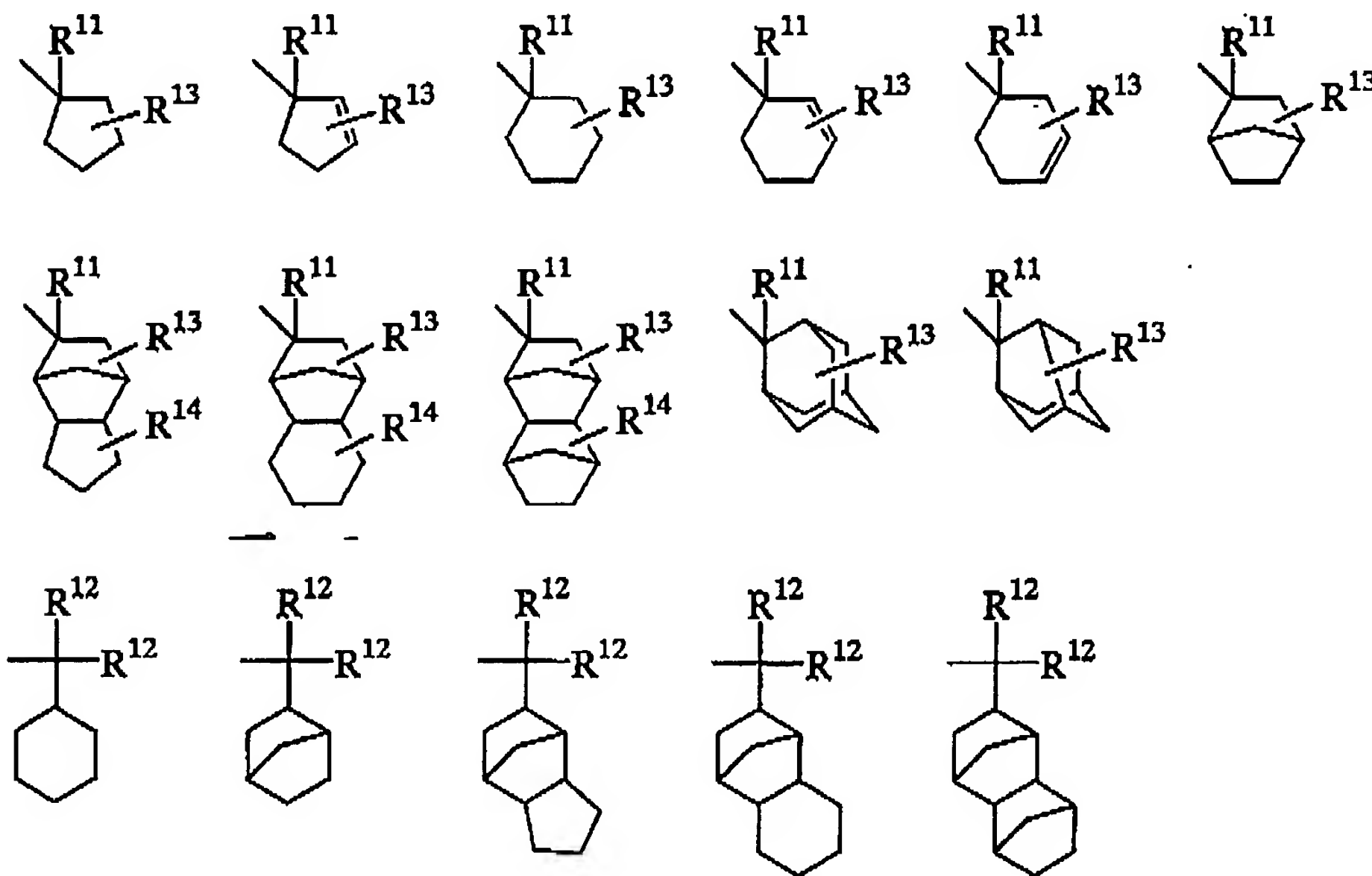
[0025]

In the general formula (5), R^8 , R^9 and R^{10} are independently monovalent hydrocarbon groups, for example, straight, branched or cyclic alkyl groups of 1 to 20 carbon atoms, which may contain a hetero atom such as oxygen, sulfur, nitrogen or fluorine. A pair of R^8 and R^9 , a pair of R^8 and R^{10} , or a pair of R^9 and R^{10} , taken together, may form a ring with the carbon atom to which they are bonded.

[0026]

10 Examples of the tertiary alkyl group represented by the general formula (5) include tert-butyl, triethylcarbyl, 1-ethylnorbornyl, 1-methylcyclohexyl, 1-ethylcyclopentyl, 2-(2-methyl)adamantyl, 2-(2-ethyl)adamantyl, tert-amyl, 1,1,1,3,3,3-hexafluoro-2-methyl-isopropyl, and
15 1,1,1,3,3,3-hexafluoro-2-cyclohexyl-isopropyl. Other illustrative examples of the tertiary alkyl group are given below.

[0027]



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[0028]

Herein, R^{11} is a straight, branched or cyclic alkyl group of 1 to 6 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, cyclopropyl, cyclopropylmethyl, cyclobutyl, cyclopentyl and cyclohexyl. R^{12} is a straight, branched or cyclic alkyl group of 2 to 6 carbon atoms, for example, ethyl, propyl, isopropyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, cyclopropyl, cyclopropylmethyl, cyclobutyl, cyclopentyl and cyclohexyl. R^{13} and R^{14} each are hydrogen or a monovalent hydrocarbon group of 1 to 6 carbon atoms which may contain a hetero atom or a monovalent hydrocarbon group of 1 to 6 carbon atoms which may be separated by a hetero atom. The hydrocarbon groups may be straight, branched or cyclic. The hetero atom is an oxygen, sulfur or nitrogen atom, which is contained or intervenes in the form of -OH, -OR¹⁵, -O-, -S-, -S(=O)-, -NH₂, -NHR¹⁵, -N(R¹⁵)₂, -NH-, or -NR¹⁵- wherein R¹⁵ is an alkyl group of 1 to 5 carbon atoms. Illustrative examples of R^{13} and R^{14} include methyl, hydroxymethyl, ethyl, hydroxyethyl, propyl, isopropyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, methoxy, methoxymethoxy, ethoxy and tert-butoxy.

[0029]

Other useful acid labile groups are trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms. Exemplary trialkylsilyl groups are trimethylsilyl, triethylsilyl and dimethyl-tert-butylsilyl.

[0030]

As long as the monomer of the general formula (1) or (2) is used as the main component, another styrene monomer may be copolymerized in the invention. In order for living polymerization of the above monomers to take place, polymerization initiators are often used, preferably organometallic compounds. Exemplary organometallic compounds are organic alkali metal compounds including n-butyl lithium, sec-butyl lithium, tert-butyl lithium, sodium naphthalene, sodium anthracene,

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α -methylstyrene tetramer disodium, cumyl potassium, cumyl cesium, phenyl magnesium bromide, phenyl magnesium chloride, ethyl magnesium bromide, ethyl magnesium chloride, n-butyl magnesium bromide, and n-butyl magnesium chloride.

5 [0031]

Living polymerization of the above monomers is generally effected in an organic solvent. Examples of suitable organic solvents include cyclic ethers, aromatic hydrocarbons and aliphatic hydrocarbons, such as benzene, 10 toluene, tetrahydrofuran, dioxane, tetrahydropyran, dimethoxyethane, n-hexane, and cyclohexane. These organic solvents may be used alone or in admixture.

[0032]

For living polymerization of the monomer of the 15 general formula (1), optimum reaction conditions including the type of living polymerization initiator and the concentration of the monomer in an organic solvent vary with a particular functional group selected for the monomer. It is recommended that the optimum reaction conditions be 20 determined by carrying out a preliminary experiment. In general, the concentration of the monomer in an organic solvent is preferably 1 to 50% (% is by weight, hereinafter) more preferably 5 to 30%.

[0033]

25 Polymerization of the monomer of the general formula (1) or (2) can be carried out by evacuating the reaction system and agitating a solution of the monomer in an organic solvent in vacuum or in a replacement atmosphere of inert gas such as nitrogen. The reaction temperature may be 30 selected in the range of -100°C to the boiling point. For instance, the preferred reaction temperature is -100°C when tetrahydrofuran is used as the solvent, and room temperature when benzene is used. If anions at ends of polymerization are unstable enough to retard polymerization at an initial 35 stage of polymerization, a small amount of a polymerizable compound capable of enhancing the stability of anions, for example, styrene or t-butoxystyrene may be added

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simultaneously with a catalyst and thereafter, the monomer of the general formula (1) or (2) be added for polymerization. In this event, one end of the polymer being formed is composed of recurring units of styrene or
5 t-butoxystyrene. Near the end of derivative polymerization, the reaction can be terminated by adding a stopper such as methanol, water or methyl bromide to the reaction solution. Further, if necessary, the fluorinated polymer may be worked up and isolated by adding methanol to the reaction mixture
10 for causing the fluorinated polymer to precipitate, followed by washing and drying. The reaction solution generally contains unreacted reactants and by-products as impurities. If the fluorinated polymer produced is used as the base in resist materials for VLSI microfabrication without further
15 treatment, the impurities can have detrimental effects on the wafer processing process. For this reason, sufficient treatment to remove a low molecular fraction and impurities should preferably be carried out.

[0034]

20 The fluorinated polymer thus obtained is monodisperse or has a polydispersity index (M_w/M_n) of 1 to 1.20, satisfying the desired narrow molecular weight distribution. With a polydispersity index of more than 1.20, the effect of living polymerization is lessened, allowing a low molecular
25 weight fraction to incur an unstable state during the patterning process.

[0035]

... The yield of polymerization is approximately 100% based on the monomer fed to the reaction system. The
30 molecular weight of the polymer is readily calculated from the weight of the monomer used and the number of moles (molecular weight) of the polymerization initiator. The number average molecular weight (M_n) is determined from the measurement of a membrane osmometer. By further performing
35 characterization by gel permeation chromatography (GPC), it can be evaluated whether the fluorinated polymer has the desired polydispersity index.

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[0036]

The fluorinated polymer of the invention is useful as a base polymer in chemically amplified photoresist compositions whose formulation is not critical. In one exemplary resist composition, there are formulated the fluorinated polymer of the invention as a base, an onium salt cationic photoinitiator, an inert organic solvent, a quencher and optional components. The onium salt cationic photoinitiator is to generate a strong acid upon exposure to light. When a resist film comprising the fluorinated polymer of the invention and the onium salt is processed by a wafer stepper, the onium salt is decomposed to generate a strong acid which causes the acid labile groups in the fluorinated polymer to be cleaved whereby the fluorinated polymer turns to be alkali soluble. The amount of the onium salt cationic photoinitiator blended is preferably 0.01 to 20%, more preferably 1 to 10% of the entire resist composition.

[0037]

On use, the resist composition is generally dissolved in a several fold volume of an organic solvent to form a resist solution which is ready to apply. The suitable organic solvent is the one in which the resist components including the living polymer of the invention are fully soluble and which allows a resist coating to spread uniformly. Illustrative, non-limiting, examples of the organic solvent include ketones such as cyclohexanone and methyl-2-n-amylketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; and esters such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate,

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tert-butyl acetate, tert-butyl propionate, and propylene glycol mono-tert-butyl ether acetate. The solvent is preferably used in an amount of about 200 to 5,000 parts per 100 parts of the resin.

5 [0038]

Preferred quenchers used herein include ammonia, primary, secondary and tertiary aliphatic amines, mixed amines, aromatic amines, heterocyclic amines, carboxyl group-bearing nitrogenous compounds, sulfonyl group-bearing
10 nitrogenous compounds, hydroxyl group-bearing nitrogenous compounds, hydroxyphenyl group-bearing nitrogenous compounds, alcoholic nitrogenous compounds, amide derivatives, and imide derivatives. The quencher is preferably used in an amount of 0.01 to 2 parts, more
15 preferably 0.01 to 1 part per 100 parts of the resin. Less than 0.01 part of the quencher is ineffective to its purpose whereas more than 2 parts of the quencher may lower the sensitivity of the resist composition.

[0039]

20 For the use, light exposure and processing of the resist composition, well-known lithographic techniques may be employed. By way of light exposure through a photomask using a stepper or scanner, the resist composition can be processed into fine patterns which are suitable in a wide
25 range of applications including semiconductor devices and displays. For development, conventional positive developers may be used.

[0040]

The fluorinated polymers of the invention are suited
30 as a base polymer in resist compositions to be exposed to ultraviolet radiation of 157 nm to 254 nm, especially suited for micropatterning in the advanced semiconductor technology. The polymers can also comply with the lithography using electron beams and x-rays.

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[0041]

[Embodiment of the Invention]

Examples of the invention are given below by way of illustration and not by way of limitation.

5 [0042]

[Example 1]

A monomer, 3,5-di[2-t-butoxy-2,2-bistrifluoromethyl]-methyl-styrene was previously treated with CaH_2 to remove water and impurities, then purified by using benzophenone sodium and distillation. A 1-liter flask was charged with 600 ml of tetrahydrofuran as a solvent and 3.5×10^{-3} mol of sec-butyl lithium as a polymerization initiator. To this mixture, 36 g of the purified 3,5-di[2-t-butoxy-2,2-bistrifluoromethyl]methyl-styrene diluted with 100 ml of tetrahydrofuran at -78°C was added. Polymerization reaction was conducted for 1 hour whereupon the solution turned red. Methanol was added to the reaction solution to terminate polymerization. The reaction solution was poured into methanol whereupon the polymer precipitated. The precipitate was separated, worked up and dried, yielding 36 g of a white polymer.

[0043]

The polymer had a number average molecular weight (M_n) of 1.1×10^4 /mole as determined by GPC using polystyrene standards. The polydispersity index (M_w/M_n) was 1.17. This is designated Polymer 1.

[0044]

[Example 2]

A monomer, 3,5-di[2-t-butoxy-2,2-bistrifluoromethyl]-methyl- α -methylstyrene was previously treated with CaH_2 to remove water and impurities, then purified by using benzophenone sodium and distillation. A 1-liter flask was charged with 600 ml of tetrahydrofuran as a solvent and 3.5×10^{-3} mol of sec-butyl lithium as a polymerization initiator. To this mixture, 37 g of the purified 3,5-di[2-t-butoxy-2,2-bistrifluoromethyl]methyl- α -

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methylstyrene diluted with 100 ml of tetrahydrofuran at -78°C was added. Polymerization reaction was conducted for 1 hour whereupon the solution turned red. Methanol was added to the reaction solution to terminate polymerization. The
5 reaction solution was poured into methanol whereupon the polymer precipitated. The precipitate was separated, worked up and dried, yielding 37 g of a white polymer.

[0045]

The polymer had a number average molecular weight (M_n)
10 of 1.13×10^4 /mole as determined by GPC using polystyrene standards. The polydispersity index (M_w/M_n) was 1.07. This is designated Polymer 2.

[0046]

[Example 3]

15 Monomers, 3,5-di[2-ethoxyethoxy-2,2-bis(trifluoromethyl)methyl]methylstyrene and 3,5-di[2-*t*-butoxy-2,2-bis(trifluoromethyl)methyl]methylstyrene each were previously treated with CaH_2 to remove water and impurities, then purified by using benzophenone sodium and distillation. A
20 1-liter flask was charged with 600 ml of tetrahydrofuran as a solvent and 3.5×10^{-3} mol of sec-butyl lithium as a polymerization initiator. To this mixture, 19 g of the purified 3,5-di[2-ethoxyethoxy-2,2-bis(trifluoromethyl)methyl]methylstyrene and 18 g of the purified 3,5-di[2-*t*-butoxy-
25 2,2-bis(trifluoromethyl)methyl]methylstyrene diluted with 100 ml of tetrahydrofuran at -78°C was added. Polymerization reaction was conducted for 1 hour whereupon the solution turned red. Methanol was added to the reaction solution to terminate polymerization. The reaction solution was poured into
30 methanol whereupon the polymer precipitated. The precipitate was separated, worked up and dried, yielding 36 g of a white polymer.

[0047]

The polymer had a number average molecular weight (M_n)
35 of 1.2×10^4 /mole as determined by GPC using polystyrene

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standards. The polydispersity index (Mw/Mn) was 1.15. This is designated Polymer 3.

[0048]

[Example 4]

5 In 1000 ml of acetone was dissolved 30 g of Polymer 1. A small amount of conc. hydrochloric acid was added to the solution, which was stirred for 7 hours at 20°C. The reaction solution was poured into water whereupon the polymer precipitated. The precipitate was washed and dried,
10 yielding 23 g of the polymer. On analysis by GPC and ¹H-NMR where the peak attributable to t-butoxy group was not observed, the polymer was identified to be poly-3,5-di[2-hydroxy-2,2-bistrifluoromethyl]methyl-styrene having a number average molecular weight (Mn) of 8800 and a
15 polydispersity index (Mw/Mn) of 1.17.

[0049]

In 200 ml of pyridine was dissolved 20 g of the above polymer. With stirring at 45°C, 13.0 g of di-tert-butyl dicarbonate was added. Reaction was effected for one hour,
20 after which the reaction solution was added dropwise to 3 liters of water, yielding a white solid. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. Filtration and vacuum drying yielded a polymer. On analysis by ¹H-NMR, it was
25 found that 48% of the hydrogen atoms of hydroxyl groups on 3,5-di[2-hydroxy-2,2-bistrifluoromethyl]methyl-styrene had been replaced by t-butoxycarbonyl groups. The polymer had a number average molecular weight (Mn) of 1.2×10^4 /mole as
determined by GPC using polystyrene standards. The
30 polydispersity index (Mw/Mn) was 1.17. This is designated Polymer 4.

[0050]

[Example 5]

In 1000 ml of acetone was dissolved 30 g of Polymer 2.
35 A small amount of conc. hydrochloric acid was added to the solution, which was stirred for 7 hours at 20°C. The reaction solution was poured into water whereupon the

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polymer precipitated. The precipitate was washed and dried, yielding 24 g of the polymer. On analysis by GPC and ¹H-NMR where the peak attributable to t-butoxy group was not observed, the polymer was identified to be poly-3,5-di[2-hydroxy-2,2-bistrifluoromethyl]methyl- α -methylstyrene having a Mw of 8800 and a Mw/Mn of 1.17.

[0051]

In 200 ml of pyridine was dissolved 20 g of the above polymer. With stirring at 45°C, 13.0 g of di-tert-butyl dicarbonate was added. Reaction was effected for one hour, after which the reaction solution was added dropwise to 3 liters of water, yielding a white solid. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. Filtration and vacuum drying yielded a polymer. On analysis by ¹H-NMR, it was found that 40% of the hydrogen atoms of hydroxyl groups on 3,5-di[2-hydroxy-2,2-bistrifluoromethyl]methyl- α -methylstyrene had been replaced by t-butoxycarbonyl groups. The polymer had a number average molecular weight (Mn) of 1.23×10^4 /mole as determined by GPC using polystyrene standards. The polydispersity index (Mw/Mn) was 1.07. This is designated Polymer 5.

[0052]

[Example 6]

In 1000 ml of acetone was dissolved 30 g of Polymer 3. Then 5 g of oxalic acid and 10 g of water was added to the solution, which was stirred for 20 hours at 40°C. The reaction solution was poured into water whereupon the polymer precipitated. The precipitate was washed and dried, yielding 26 g of the polymer. On analysis by GPC and ¹H-NMR, the peak attributable to ethoxyethoxy group was not observed. The polymer was identified to be poly-3,5-di[2-t-butoxy-2,2-bistrifluoromethyl]methyl-styrene-co-3,5-di[2-hydroxy-2,2-bistrifluoromethyl]methyl-styrene in a ratio of 0.52:0.48 having a number average molecular weight (Mn) of 1.03×10^4 /mole as measured by GPC using polystyrene standards

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and a polydispersity index (M_w/M_n) of 1.15. This is designated Polymer 6.

[0053]

[Application Example]

5 A resist solution was prepared by dissolving 3 g of each polymer obtained in Examples 4, 5 and 6, 0.12 g of triphenylsulfonium nonafluorobutanesulfonate (photoacid generator) and 0.006 g of tributylamine (basic quencher) in 25 ml of propylene glycol monomethyl ether acetate. The
10 solution was filtered through a filter having a pore size of 0.2 μm . The resist solution was spin coated onto a silicon wafer having a 55-nm coating of DUV-30 (Brewer Science) formed thereon, and baked on a hot plate at 120°C for 90 seconds to form a resist film of 300 nm thick.

15 [0054]

Using an excimer laser stepper (Nikon Corporation, NSR-S203B, NA = 0.68, σ = 0.75, 2/3 annular illumination), the resist film was exposed to laser beams. The resist film was baked at 110°C for 90 seconds immediately after exposure
20 and developed with a 2.38% aqueous solution of tetramethylammonium hydroxide for 60 seconds. There was obtained a positive pattern having a resolution of 0.13 μm and a line to space ratio of 1:1.



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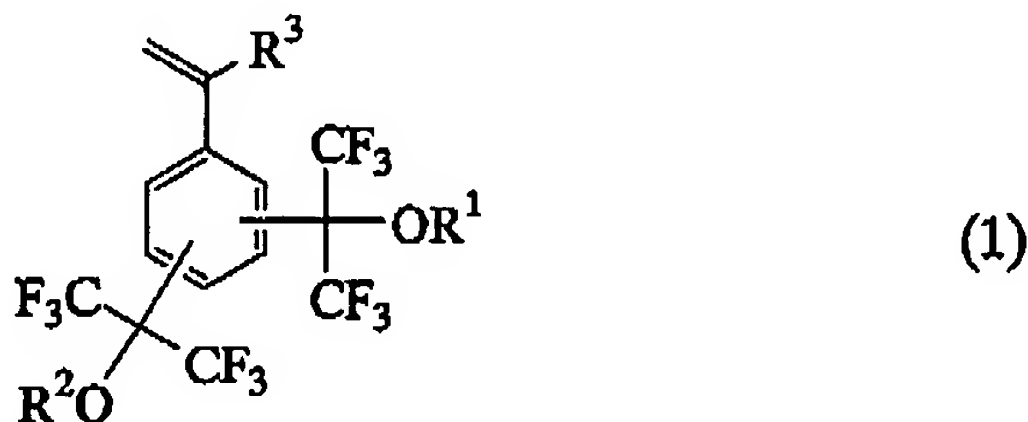
[ABSTRACT]

[Problem]

For the preparation of polymers for use in the UV wavelength regions, many processes utilizing radical polymerization and vinyl addition polymerization have been reported. The polymers obtained by these processes have a wide molecular weight distribution or polydispersity index. When such a polymer is used in resist, a low molecular weight fraction of the polymer gasifies. As a result, the patterning process is reproducible with difficulty, often forming uneven patterns.

[Means for Solution]

A fluorinated polymer obtained by living anion polymerization of a monomer having the general formula (1):



15

wherein R^1 and R^2 each are an acid labile group and R^3 is hydrogen or methyl, and having a polydispersity index of 1 to 1.20.

[Selected Drawing] none

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